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ESTIMATING THE SIZE OF POLAR AND APOLAR NANOPARTICLE AGGLOMERATES IN A FLUIDIZED BED

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ABSTRACT

We present a model to estimate the nano-agglomerate sizes in fluidized beds. The model only needs four input parameters: the particle size, density, Hamaker coefficient and type of surface (hydrophobic/hydrophilic) of the nanoparticles. It has been validated with 34 sizes reported in literature, predicting the values more accurately than any other model.

INTRODUCTION

Fluidization is emerging as a promising but challenging technique for processing of nanoparticles, for instance, to produce coated nanoparticles (1). Nanoparticles do not fluidize individually but form agglomerates due to strong interparticle forces, dominant at the nano-scale. The type of fluidization and transport phenomena inside the agglomerates strongly depend on the agglomerates structure and size, two variables in turn related to the forces present between particles and agglomerates.

Several researchers have studied the structural properties (2-5) and size (6, 7) of fluidized agglomerates. It is commonly accepted that they are fractal structures, i.e. the number of units in each agglomerate scales as

$$N_0 = k\left(\frac{d}{d_0}\right)^{D_f} \quad (1)$$

where k is a prefactor (8) and d_0 is the size of the unit that is repeated N_0 times to form the fractal with size d and fractal dimension D_f. The fractal dimension is typically obtained measuring the settling velocity of individual particles (4, 5), the settling velocity of the whole fluidized bed (2), or from fluidized bed expansion measurements (3). Castellanos *et al.* (2) and Wang *et al.* (5) found a dimension ~2.5, while Nam *et al.* (3) found a value of ~2.6. Quintanilla *et al.* (4) reported a fractal dimension 2.6 for primary agglomerates and 2.3 for complex agglomerates.

Models to predict the average size of fluidized agglomerates are reviewed in (9, 10). Unfortunately, most of them have been applied over a limited range of conditions and require measuring a number of variables (9). To obtain a simple

model to predict the agglomerate size, Valverde and Castellanos (9) propose a balance between attractive forces and weight of the agglomerates (Bond number).

$$\mathrm{Bo} \equiv \frac{F_{attractive}}{W} \qquad (2)$$

This equilibrium criterion was also used by Chaouki *et al.* (11). Forces such as those due to bubbles or collisions between agglomerates are neglected. This model is able to predict the order of magnitude of fluidized agglomerates, but it underestimates the sizes even choosing a Hamaker coefficient of $1.50 \cdot 10^{-19}$ J for all the powders (the value for amorphous silica is $6.60 \cdot 10^{-20}$ J (12, 13)). Moreover, the model is hardly dependent on the particle size and density, predicting a size of ~180 μm for all types of dry non-centrifuged powders.

In this work we provide a new model to estimate the size of fluidized agglomerates based on the equilibrium criterion used by Chaouki *et al.* (11) Valverde and Castellanos (9) (Bo=1). Our model keeps the simplicity of Valverdes but predicts agglomerate sizes much more accurately, by adapting an alternative approach for calculating $F_{attractive}$.

MODEL

As Yao *et al.* (14) showed and it is broadly accepted, fluidized agglomerates present a hierarchical structure. First, individual nanoparticles link to form sub-agglomerates or networks with a size of few hundred nanometers. These sub-agglomerates form larger agglomerates called primary agglomerates, and finally, these primary agglomerates form the largest structures known as complex agglomerates. Complex agglomerates have a size d^{**} of a few hundreds of microns, while the size d^{*} of primary agglomerates ranges from 1 to 100 μm (14). To predict d^{**}, we will consider that the complex agglomerates are formed by identical primary agglomerates with size d^{*}=35 μm, the same value used by Valverde and Castellanos (9), inferred from SEM measurements shown by Nam *et al.* (3). We will ignore the first hierarchical level, so we will consider that the primary agglomerates are formed by individual nanoparticles instead of individual sub-agglomerates. To determine d^{**} is necessary first to estimate the force between two primary agglomerates, this will be done modeling the surface of the primary agglomerates as will be explained next.

Surface modeling

Matsuda *et al.* (15) observed that the agglomerates formed by smaller nanoparticles have smoother surface and are stronger than the agglomerates formed by larger nanoparticles. In this work we will express that observation considering that the contact area between two primary agglomerates is composed by particles perfectly packed, in a blackberry fashion. Under this assumption the primary agglomerates will be considered as porous spheres with semi-spherical asperities of size d_p separated by a distance $\lambda = d_p$ (Fig. 1).

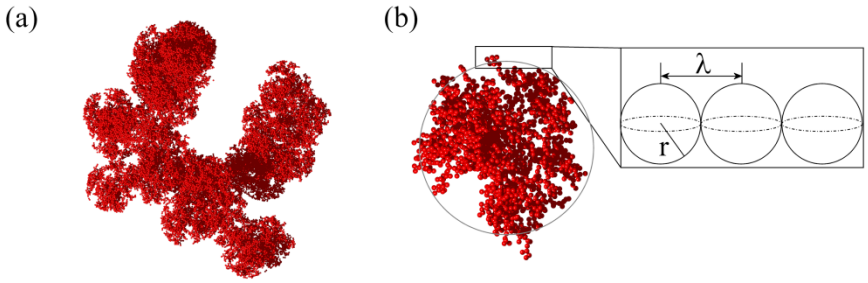

Fig. 1. (a) Complex agglomerate formed by primary agglomerates. (b) Detail of the surface a each primary agglomerate.

The interaction between a smooth sphere and a rough plane has been already modeled by different authors (16-19). In this work we will use Rabinovich's model (18) to describe the interaction between primary agglomerates (Eq. 3).

$$F_{ad} = \frac{A_H d^*}{12 H_0^2}\left[\frac{1}{1+\left(\frac{16 d^* k_1 \mathrm{rms}}{\lambda^2}\right)} + \frac{1}{2\left(1+\frac{k_1 \mathrm{rms}}{H_0}\right)^2}\right] \quad (3)$$

where H_0 is the minimum interparticle distance =0.4 nm (20), k_1 = 1.817, rms= $0.0172\lambda^2/r$ and r is the radius of the asperities, in this case the radius of the nanoparticles. Eq. (3) is applicable if λ >> 15.4rms and $\lambda << (16 k_1 d^* \mathrm{rms})^{0.5}$. The factor 2 that appears in the denominator of the second term is absent in the original model. This is because the second term of the original model describes the indirect interaction between a plane and a sphere separated by an average distance $H_0 k_1$rms. Dividing that term by 2 gives the indirect interaction between two spheres of size d^* separated by a distance $H_0 k_1$rms. The first term describes the direct contact between one agglomerate and the asperities of the other agglomerate. When two agglomerates with asperities come in contact, the interaction plane will depend on how the asperities connect. If the asperities of the agglomerates are facing up the interaction is minimum, while if the bumps of one agglomerate are inside the pitches of the other the attraction is maximum. In reality, the attraction will be between these two cases. To get an averaged interaction plane we will simply consider that one of the agglomerates is smooth, while the other has a surface with asperities.

Expressing Eq. (3) in a more convenient way, we have

$$F_{ad} = \frac{A_H d^*}{24 z_{eq}^2} \quad (4)$$

where

$$z_{eq} = H_0 \left[\frac{2}{1+\left(\frac{16 d^* k_1 \mathrm{rms}}{\lambda^2} \right)} + \frac{1}{\left(1+\frac{k_1 \mathrm{rms}}{H_0} \right)^2} \right]^{-0.5} \quad (5)$$

If nanoparticle diameter d_p is much smaller than the simple-agglomerate diameter d^*, the total interaction is dominated by the indirect agglomerate-agglomerate interaction. This is opposite to previous works (e.g., (9)), where it is claimed that the interaction is dominated by the direct contact asperity-agglomerate. The later conclusion appears when it is assumed that the agglomerates are solid bodies with asperities with a size ~0.2 μm, the typical size of the asperities observed in micron-sized particles.

It is important to remark that this model assumes that the contact area between primary agglomerates is formed by perfectly packed particles. This seems in conflict with the assumption that the primary agglomerates are fractals. This is actually not the case since this characteristic only refers to the contact area and it serves just to define the average separation between the agglomerates.

Hamaker coefficient

The next step is to correct the Hamaker coefficient to account for the porosity of the agglomerates. We will simply consider the agglomerates as a cluster of atoms with an atomic load that depends on the porosity. Also, we will ignore effects due to atomic screening and changes of the dielectric function near to the particle surface. The Hamaker coefficient can be then expressed according to the two-body summation as (21)

$$A_H = f(\alpha_0, \omega_0) n^2 \quad (6)$$

where $f(\alpha_0,\omega_0)$ depends on the type of atoms in the cluster and n is the number density. The van der Waals interaction between two porous agglomerates of size d^* and density ρ^* can be accordingly written as

$$F_{vdW} = \frac{A_H d^* \left(\rho^* / \rho_p \right)^2}{24 z_{eq}^2} \quad (7)$$

where A_H is the Hamaker coefficient of the non-porous material. To the best of our knowledge, this is the first time that the porosity of the agglomerate is included in the estimation of the interaction between agglomerates.

Hydrogen bridges

As shown recently by Tahmasebpoor *et al.* (22), the hydrogen bonds formed between dry polar particles substantially increase the interparticle attraction. This contribution of hydrogen bonds between dry polar particles to the interparticle attraction was not taken into account before in fluidization literature. In line with the results reported in (22), this phenomenon will be included in the model considering that each primary agglomerate provides N_p particles of size d_p to participate in the hydrogen bonding. Each particle has a concentration of active hydroxyl groups on the surface C_{OH} and it exposes a fraction X of its surface to the bonding (Fig. 2a). Then, the number of hydrogen bonds between two agglomerates would be $N_{bonds} = N_p X \pi d_p^2 C_{OH}$. To calculate N_p we have to take into account the curvature of the primary agglomerates and the length scale of the hydrogen bond h_{max}. If the primary agglomerates are spherical, the N_p particles would be placed on a spherical cap of area $A_{cap} = \pi/2 d^*(h_{max} - H_0)$ (Fig. 2a).

To calculate the number of particles in the cap we will consider that the space between them (black space in Fig. 2b) is negligible compare to their surface (gray space in Fig. 2b). Then, $N_p = \frac{A_{cap}}{\pi/4 d_p^2}$ and $N_{bonds} = 2X\pi(h_{max} - H_0)d^* C_{OH}$ independent on d_p. If the average strength of the each hydrogen bond is f_{OH} the total force between two agglomerates due to hydrogen bonding is

$$F_{OH} = \alpha d^* \qquad (8)$$

where $\alpha = 2X\pi(h_{max} - H_0)C_{OH} f_{OH}$. Typical values are C_{OH}=2-5 OH/nm^2 and f_{OH}=4 pN. For the sake of simplicity we will consider that α is the same for all polar particles.

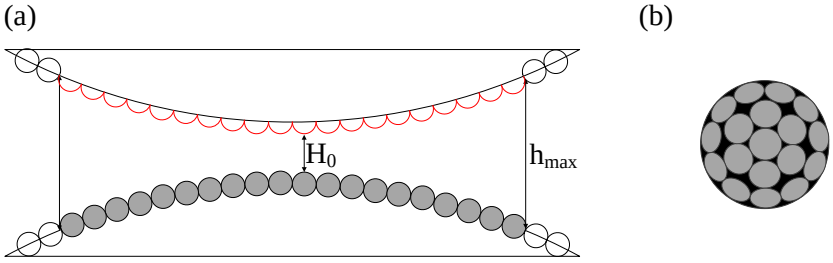

Fig. 2. (a) Effect of the hydrogen bond between the hydroxyl groups of the polar nanoparticles. h_{max} is the maximum length scale of the hydrogen bond. The gray particles are in the area of the agglomerate $A_{cap} = \pi/2 d^*(h_{max} - H_0)$ actively participate in the bonding. Each active particle provides a fraction X of its surface to the hydrogen bond. (b) Top view. A possible configuration of hemispherical asperities in a spherical cap.

As explained previously, we have adopted the same equilibrium criterion between forces that Valverde and Castellanos (9) and Chaouki *et al.* (11), i.e. Bond number equals to one. If the two only attracting forces are F_{vdW} and F_{OH} and the only separating force is the agglomerate weight, the size of the average agglomerates will be given simply by Eq. (9).

$$Bo \equiv \frac{N_c \left(F_{vdW} + F_{OH} \right)}{\frac{\pi}{6} (d^{**})^3 \rho^{**} g} = 1 \qquad (9)$$

where N_c is the number of links between primary agglomerates that is necessary to separate to break the complex agglomerate somewhere. We find from simulations on particle-cluster diffusion limited aggregation (PCDLA) and cluster-cluster diffusion limited aggregation (CCDLA) N_c ~1.

Substituting Eq. (7) and Eq. (8) in Eq. (9) and knowing that in a hierarchical agglomerate

$$\frac{\rho^*}{\rho_p} = k_0 \left(\frac{d^*}{d_p} \right)^{D_0 - 3} \text{ and } \frac{\rho^{**}}{\rho^*} = k_1 \left(\frac{d^{**}}{d^*} \right)^{D_1 - 3} \qquad (10)$$

the average size of the complex agglomerates is

$$d^{**} = \left(\frac{N A_H d^{*(D_1 + D_0 - 5)} + N \hat{\alpha} z_{eq}^2 d_p^{(2D_0 - 6)} d^{*(D_1 - D_0 + 1)}}{z_{eq}^2 g d_p{}^{(D_0 - 3)} \rho_p} \right)^{1/D_1} \qquad (11)$$

where $\hat{\alpha} = \frac{24\alpha}{k_0^2}$ and $N = \frac{N_c k_0}{4\pi k_1}$.

For apolar particles $\hat{\alpha} = 0$ and Eq. (11) simplifies considerably. Note that the interaction between apolar particles is hardly dependent on the size of the primary agglomerates d^* if $D_1 \sim D_0 \sim 2.5$, which are typical values reported (1, 3). Moreover, if $D_1 + D_0 < 5$ the interaction decreases with an increase of d^*. This is related to the dependence of the agglomerate density on the fractal dimension. If the fractal dimension is low, an increase in d^* would lead to a strong decrease in ρ^* (see Eq. (7)), decreasing the total interaction. If the agglomerates were rigid bodies, then $D_1 = D_0 = 3$ and the interaction would increase linearly with d^*, like in Eq. (4).

On the contrary, d^* always affects to the interaction between polar particles. This happens because the larger the agglomerates are, the more hydrogen bonds between them are formed.

RESULTS

The model has been applied with the parameter shown in Tables 1 and 2; the results are shown in Fig. 3. Note that N must be the same for all types of powders since it is related to the structure of the complex agglomerates. N and N_c are related through the prefactors k_0 and k_1, which depend on the fractal structure (8) although most of the authors consider them 1 (3, 4, 23). If $k_0 = k_1 = 1$, the value predicted by the model is N_c = 1.38, consistent with the value found in PCDLA and CCDLA mechanisms.

Table 1 Parameters used in the model known from literature.

Parameter	Value
d^*	35 μm (3, 9)
D_0	2.6 (4)
D_1	2.3 (4)
A_H SiO_2	6.60e-20 J (12, 13)
A_H TiO_2	1.49e-19 J (12, 13)
A_H Al_2O_3	1.45e-19 J (12, 13)

Table 2 Chosen parameters.

Parameter	Value
N for all the particles	0.11
$\hat{\alpha}$ for apolar particles	0 N/m
$\hat{\alpha}$ for polar particles	0.04 N/m

The proposed model successfully approximate the size of the agglomerates for most of the powders reported even though it just uses two fitting parameters N and $\hat{\alpha}$, both of them with a clear physical meaning. It is important to point out that the sizes reported in literature are very scattered, finding large differences between sizes for the same nanopowders. Thus, it is questionable to judge the model only on the goodness of the fitting. Nevertheless, what is remarkable in this model is that, although it is highly sensitive to the Hamaker coefficient, particle density particle size and type of surface (polar or apolar) the predicted sizes are unbiased. A systematic error as a function of the particle size, density, Hamaker coefficient has not been found. The average prediction error of the proposed model is 19 %, while in the model proposed by Valverde and Castellanos (9) it is 33 %.

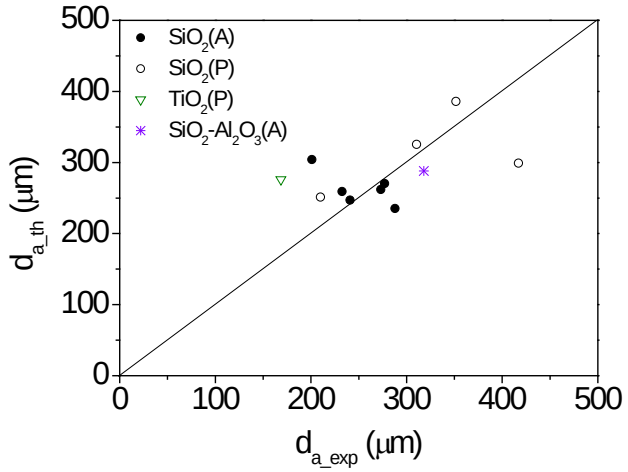

Fig. 3. Agglomerate sizes predicted by the model shown in Eq. (11). The 12 data plotted have been obtained from 34 experimental agglomerate sizes reported in literature in dry environments, most of the values are collected from (9). Each data plotted has been obtained averaging the sizes reported for the same particle size, density, material and surface properties. (A) means apolar surface (hydrophobic) and (P) polar surface (hydrophilic).

CONCLUDING REMARKS

In this work we have proposed a simple model to predict the size of the agglomerates formed in a fluidized bed of nanoparticles. The model only needs the size, density, Hamaker coefficient and type of surface (hydrophilic/hydrophobic) of the nanoparticles as input parameters. Additional forces like capillary or those due to the action of a microjet can be easily implemented in this model. The model works under the assumption that $d^* >> d_p$; therefore, it cannot be directly applied to estimate the sizes of the agglomerates formed by micro-sized particles.

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